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(54) **Substituted metallocene catalyst for the (co)polymerization of olefins**

Substituierte Metallocen-Katalysator für die Olefinpolymerisation

Catalyseur à base de métallocène substitué pour la (co)polymérisation d'oléfines

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(73) Proprietor: **ENICHEM S.p.A.**
20124 Milano (IT)

(72) Inventors:
• **Santi, Roberto**
Novara (IT)
• **Borsotti, Giampiero**
Novara (IT)
• **Quercl, Cecilia**
28100 Novara (IT)
• **Gila, Lilliana**
Cameriano (Novara) (IT)

• **Proto, Antonio**
Novara (IT)

(74) Representative: **De Gregori, Antonella**
Ing. Barzano & Zanardo Milano S.p.A.
Via Borgonuovo 10
20121 Milano (IT)

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COMMUNICATIONS, vol. 15, no. 12, 1 December
1994, pages 923-928, XP000477618 TIAN J ET
AL: "ETHYLENE POLYMERIZATION WITH
CATALYST SYSTEMS BASED ON
METALLOCENES WITH VARYING STERIC
HINDRANCE AND METHYLALUMINOXANE"

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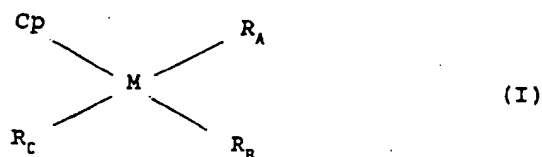
EP 0 791 607 B1

Description

[0001] The present invention relates to a substituted metallocene catalyst for the (co)polymerization of olefins.

[0002] More specifically, the present invention relates to a substituted metallocene complex of a metal of group 4 of the periodic table of elements, and a catalyst suitable for polymerizing or copolymerizing ethylene and/or other α -olefins, consisting of this catalyst combined with an appropriate co-catalyst. The present invention also relates to a process for the polymerization of α -olefins in the presence of this catalyst to obtain polyolefins with high molecular weights.

[0003] It is generally known in the art that ethylene, or alpha-olefins in general, can be polymerized by processes at low or medium pressure with catalysts based on a transition metal, generally known as catalysts of the Ziegler-Natta type. More recently, a particular of these catalysts which are active in the polymerization of olefins, has been found, consisting of a combination of an organic oxyderivative of aluminium (commonly called aluminoxane) with an η^5 -cyclopentadienyl derivative of a metal normally selected from titanium, zirconium or hafnium (group 4 of the periodic table), also commonly called metallocene, definable in its more general form with the following formula (I):



wherein M represents a metal of group 4 of the periodic table of elements, formally in the oxidation state +4, and is preferably titanium or zirconium; R_A and R_B each independently represent a group of an anionic nature such as, for example, a hydride, a halide, a phosphonated or sulfonated anion, an alkyl or alkoxy group, an aryl or aryloxy group, an amide group, a silyl group, etc.; Cp independently represents a ligand of the η^5 -cyclopentadienyl type and is generally selected from η^5 -cyclopentadienyl, η^5 -indenyl, η^5 -fluorenyl and their derivatives variously substituted; R_C , independently of the nature of the other substituents, can have one of the meanings of either the ligand Cp, or the R_A or R_B groups. Particular "bridged" metallocenes are also known in the known art, wherein two Cp groups, the same or different, are bound by a divalent radical normally containing at least one carbon atom, and possibly also heteroatoms such as, for example, nitrogen, oxygen, silicon or germanium. For a typical example of a known method for the preparation of the above compounds, reference should be made, as an example, to the description of H. Sinn, W. Kaminsky, in Adv. Organomet. Chem., vol. 18 (1980), page 99 and to U.S. patent 4.542.199.

[0004] These catalysts generally have a high catalytic activity and a certain versatility when applied to the preparation of polyolefins with specific characteristics, especially with respect to the control of the molecular weight dispersion, normally more limited than the classical Ziegler-Natta catalysts, or the stereoselectivity during the polymerization of α -olefins, normally obtained using the above "bridged" metallocene complexes.

[0005] It has been observed however that the behaviour of the metallocene complexes is not entirely satisfactory with respect to the average molecular weight of the polyolefins obtained therewith, especially when operating with processes at a high temperature, and particularly in the copolymerization of ethylene with α -olefins to produce linear low density polyethylene (LLDPE) or olefinic elastomers (EPC). On the other hand, there is a great necessity for polymerization processes capable of producing polyolefins with the highest possible molecular weight to be able to develop different grades of product by intervening with suitable chain transfer agents.

[0006] It is also desirable to have catalysts based on metallocene complexes with a greater thermal stability and stability to reactive agents such as air or humidity, to simplify the conservation and transfer methods and operations of the complexes themselves.

[0007] Different types of variously substituted η^5 -cyclopentadienyl binders have been examined in the known art, to improve the characteristics of the catalysts in relation to the specific applications and to overcome the above problems.

[0008] Published European patent application 576.970 describes particular bridged bis-indenyl complexes of zirconium, in which the benzene ring of each indenyl group is substituted with a phenyl or naphthyl group. Although the use of these complexes for the stereospecific polymerization of propylene is described, no important effect is mentioned with respect to the possible presence of substituents on the phenyl or naphthyl group.

[0009] Published European patent application 277.004 mentions metallocene complexes of group 4 of the periodic table, particularly zirconium, in which the cyclopentadienyl group is substituted with different radicals such as, for example, methyl, phenyl, benzyl, cyclohexyl or trifluoromethyl. The different substituents however are mentioned in general, without specifying any difference in their behaviour when the complexes containing them are used in polymerization catalysis.

[0010] U.S. patent 5.324.800 discloses the use of bis-(2-phenylpropyl) cyclopentadienylzirconium dichloride in the polymerization of ethylene. A satisfactory activity of the catalyst is only obtained however when using very high quantities of methylaluminoxane, unacceptable for many industrial uses.

[0011] Published international patent application WO 95/25.757 describes bis-(2-phenyl) indenyl catalysts for the preparation of elastomeric block polypropylene. The characteristic of these catalysts is that they have a rotation rate of the ligands on the metallo-cyclopentadiene axis which is intermediate between the insertion rate of the monomer and the chain transfer rate, so as to produce adjacent blocks of isotactic and atactic polypropylene respectively. There seems to be no indication in this document as to the role of the substituents on the ligand in relation to the stability of the complex and molecular weight of the polymer produced therewith.

[0012] EP-A 540108 discloses metallocene complexes wherein the cyclopentadienyl group is substituted with a possibly substituted aryl, specifically 2-chlorophenylindenyl and t-butylphenylindenyl complexes. Although these complexes are reported to provide polymerization catalysts with improved activity, nothing is disclosed in EP-A 540108 about the effect of electron-attraction substituents on the aryl ring.

[0013] EP-A 653433 discloses bridged bis-indenyl complexes of zirconium suitable as a catalyst for producing isotactic polypropylene, in which the six-membered ring of each indenyl group is substituted with an aryl group eventually further substituted. Trifluoromethylphenyl substituents are disclosed and exemplified. However, the synthesis of such bis-indenyl ligands include several steps and provide for a very low overall yield of the complex finally obtained.

[0014] The demand for metallocene catalysts capable of basically overcoming all the various problems mentioned above, has therefore not as yet been satisfied.

[0015] The Applicant has now found a new group of catalysts for the (co)polymerization of α -olefins, based on metallocene complexes substituted on the cyclopentadienyl ring with particular groups of an electron-attraction nature, which can be prepared with simple and convenient synthetic methods. These complexes have greater chemical and thermal stability compared to analogous non-substituted complexes, and are active, possibly in the presence of a suitable co-catalyst, in the catalysis of (co)polymerization processes of α -olefins, to produce (co)polymers with very high molecular weights.

[0016] A first object of the present invention therefore relates to a metallocene complex of a metal **M** selected from titanium, zirconium and hafnium, comprising at least one anionic group **A** containing an η^5 -cyclopentadienyl ring coordinated with the metal **M**, characterized in that the anionic group is substituted in at least one position of the cyclopentadienyl ring with a radical having the formula:



wherein:

R^6 and R^7 are independently hydrogen, halogen or a C_1 - C_4 alkyl group, preferably hydrogen or alkyl, more preferably hydrogen, and Ph^* is a C_6 - C_{14} group comprising an aromatic ring linked to $-\text{CR}^6\text{R}^7-$ and substituted with at least one and up to a maximum of three electron-attraction groups selected from fluorine, halogenated hydrocarbons radicals having from 1 to 15 carbon atoms, halogenated alkyl-silyl radicals having from 1 to 15 carbon atoms, alkoxy-carbonyl radicals, halogenated or non halogenated, having from 2 to 15 carbon atoms, and alkoxy- or arylalkoxy-alkyl radicals having from 2 to 15 carbon atoms.

[0017] A second object of the present invention relates to a catalyst for the (co)polymerization of α -olefins, comprising the above metallocene complex, possibly in contact with a co-catalyst consisting of an organo-oxygenated derivative of a metal **M'** selected from aluminium, gallium and tin.

[0018] A further object of the present invention relates to a process for the (co)polymerization of α -olefins, comprising polymerizing ethylene and/or one or more α -olefins, under suitable conditions of pressure and temperature, in the presence of the above catalyst.

[0019] Any possible further objects of the present invention are evident from the following description and examples.

[0020] The term "(co)polymerization of α -olefins" as used hereafter in the description and claims, refers to both the homo-polymerization and co-polymerization of ethylene and/or other α -olefins with more than two carbon atoms, with each other or with another ethylenically unsaturated polymerizable compound.

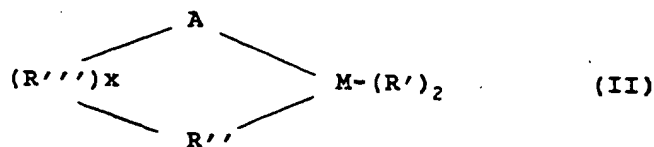
[0021] Electron-attraction groups which are suitable as substituents of the aromatic ring of the Ph^* group according to the present invention, are aprotic groups capable of polarizing the " π " orbitals of the aromatic ring with movement of the negative charge towards the substitution site. Electron-attraction groups of this type are fluorine atoms, halogenated hydrocarbon radicals, preferably fluorinated, having from 1 to 15 carbon atoms, halogenated alkylsilyl radicals, preferably fluorinated, having from 1 to 15 carbon atoms, alkoxy-carbonyl radicals, halogenated or non-halogenated, having from 2 to 15 carbon atoms, alkoxy- or aryloxy-alkyl radicals having from 2 to 15 carbon atoms, such as methoxymethyl, ethoxymethyl or trifluoromethyloxymethyl.

[0022] The electron-attraction groups present on the metallocene complexes of the present invention are preferably

fluorine and the halogenated aliphatic hydrocarbonyl or alkyl-silyl-radicals in which at least one halogen atom, preferably fluorine, is linked to a carbon atom or to a silicon atom in position 1 or 2 with respect to the aromatic ring of said Ph* group. Typical but non-limiting examples of these electron-attractor groups are trifluoromethyl, difluoromethyl, fluorodichloromethyl, trichloromethyl, 1,1-difluoroethyl, 1,1-difluoropropyl, perfluoroethyl, 1,1-difluorohexyl, trifluoromethylsilyl, trifluorosilyl, trichloromethyldifluorosilyl, acetyl, trifluoroacetyl, perfluoropropionyl, trichloroacetyl and trifluoromethoxymethyl. Trifluoromethyl and perfluoroethyl are particularly preferred.

[0023] Aromatic rings included in the definition of the Ph* groups of the present invention are the benzene ring and naphthalene groups, preferably disubstituted with two electron-attractor groups defined above. Typical examples of Ph*-(CR⁶R⁷) groups according to the present invention, with R⁶ and R⁷ equal to hydrogen, are fluorobenzyl, difluorobenzyl, 4-trifluoromethylbenzyl, 2,4-bis-(trifluoromethyl)benzyl, 3,5-bis-(trifluoromethyl) benzyl, 4-perfluoroethylbenzyl, 3,5-bis-(perfluoroethyl)benzyl, 3, 5-bis-(perfluorobutyl)benzyl.

[0024] Typical metallocene complexes in accordance with the present invention are those represented by the following formula (II) :



wherein:

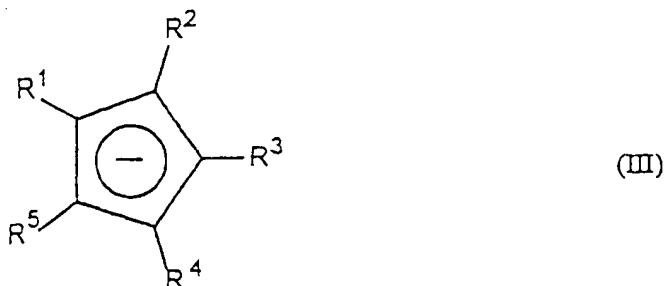
M represents a metal selected from titanium, zirconium or hafnium;

each of the two R' independently represents a substituent group selected from hydride, halide, a C₁-C₈ alkyl group, a C₃-C₁₂ alkylsilyl group, a C₅-C₈ cycloalkyl group, a C₆-C₁₀ aryl group, a C₁-C₈ alkoxy group, a C₁-C₈ carboxyl group, a C₂-C₁₀ dialkylamide group and a C₄-C₂₀ alkylsilylamide group;

R'' represents a substituent group of the same kind as the previous R' groups, independently selected from these, or a second anion containing an η⁵-cyclopentadienyl ring substituted or non-substituted, co-ordinated to the metal M, possibly selected from the substituted cyclopentadienyl anions included in the following definition of A;

R''' represents a divalent group having from 1 to 10 carbon atoms, possibly containing one or more heteroatoms, preferably O, N, P, Sn, Ge or Si, which is bridge-linked between A and R'' with covalent bonds, and R''' is preferably selected from alkylene, dialkylsilylene, diarylsilylene, dialkyl- or diarylgermylene, arylene, xylylene radicals and the like;

A is an anion containing a substituted η⁵-cyclopentadienyl ring, co-ordinated to the metal M, represented by the following formula (III):



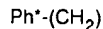
wherein:

each Rⁱ group (with i 1, 2, 3, 4 or 5) can be independently hydrogen, halogen, a C₁-C₈ alkyl group, a C₃-C₁₂ alkylsilyl group, a C₅-C₈ cycloalkyl group, a C₆-C₁₄ aryl group, a C₆-C₁₅ arylalkyl group, a C₁-C₈ alkoxy group, a C₁-C₈ carboxyl group, or two Rⁱ adjacent groups can combine with each other to form a cyclic aliphatic or aromatic structure comprising at least three, and preferably from 5 to 8 non-metallic atoms different from hydrogen and halogen; and

"x" can be 0 or 1, on the condition that when "x" is 1, the divalent R''' group is linked on one side to the A group

as a substitute of one for the R' groups having formula (III), and on the other side to the R'' group, as a substitute for any of its hydrogen atoms;

characterized in that at least one R^I in formula (III) of the A group, and possibly also in the formula of the R'' group, when this is represented by formula (III), consists of a radical having the formula:



wherein: Ph^{\bullet} is defined as above,

[0025] According to the present invention, the R^I groups having formula (II) can each independently represent, a hydride or halide, such as chloride or bromide, a C_1 - C_8 alkyl group such as, for example, methyl, ethyl, butyl, isopropyl, isoamyl, octyl, benzyl, a C_3 - C_{12} alkylsilyl group such as, for example, trimethylsilyl, triethylsilyl or tributylsilyl, a cycloalkyl group such as cyclopentyl or cyclohexyl, a C_6 - C_{10} aryl group such as phenyl or toluyl, a C_1 - C_8 alkoxy group such as, for example, methoxy, ethoxy, iso- or sec-butoxy, or a C_2 - C_{10} dialkylamide or C_4 - C_{20} alkylsilylamide group, preferably of the type represented by the general formula $-\text{NR}^8\text{R}^9$ wherein R^8 and R^9 are alkyl groups having from 1 to 4 carbon atoms, such as, for example, methyl, ethyl or butyl groups, or in the case of alkylsilylamides, alkylsilyl groups having from 3 to 6 carbon atoms, such as, for example, trimethylsilyl or triethylsilyl. The R' groups can also be joined to each other with a covalent bond to form a cyclic structure comprising the metal M . $(R^I)_2$ groups of this latter kind are, for example, 1,4-tetramethylene, ethylenedioxy or malonate groups.

[0026] Among the preferred R' groups in formula (II), chloride, methyl, benzyl and diethylamine radicals can be mentioned, although the scope of the present invention is by no means limited thereto.

[0027] In a particularly preferred embodiment the R' groups are the same as each other.

[0028] According to the present invention, the A group in formula (II) is an anion containing an η^5 -cyclopentadienyl ring having formula (III), which can be formally obtained by the extraction of a H^+ ion from the cyclopentadienyl ring of the compound having the corresponding neutral molecular structure. Preferably, A represents an η^5 -cyclopentadienyl group substituted with at least, and preferably, one $\text{Ph}^{\bullet}-(\text{CH}_2)$ group, according to what is specified above, the remaining atoms in the ring being non-substituted, or substituted with C_1 - C_8 alkyl or silylalkyl groups, or C_6 - C_{10} aryl or aryloxy groups, or C_1 - C_8 alkoxy groups. A is more preferably an η^5 -cyclopentadiene anion of formula (III) wherein R^1 is a $\text{Ph}^{\bullet}-\text{CH}_2$ group, particularly bis(fluoroalkyl)benzyl, and each of the remaining R^2 , R^3 , R^4 and R^5 are independently hydrogen or methyl.

[0029] The complexes and catalysts deriving from these however also fall within the scope of the present invention, in which group A is a cyclopentadienyl ring condenses with other cyclic structures, as in the case, for example, of the indenyl group, 4,5,6,7-tetrahydroindenyl or fluorenyl, as such or substituted as previously specified for non-condensed cyclopentadiene.

[0030] As previously defined, R'' in formula (II) can represent either a group included in the above definiene group (generally indicated herein also with the abbreviation C_p) of the type commonly known in the art. More specifically, this C_p group can represent an anion deriving from cyclopentadiene, indene or fluorene, or from a derivative of one of the above compounds, in which one or more carbon atoms of the molecular skeleton (comprised or not comprised in the cyclopentadienyl ring), are substituted with C_1 - C_8 alkyl or silylalkyl groups, or C_6 - C_{15} aryl or aryloxy groups, or C_6 - C_{15} arylalkyl groups, or C_1 - C_8 alkoxy groups. This C_p group can also be condensed with one or more other aromatic rings as in the case, for example, of 4,5-benzoidindenyl.

[0031] Typical but non-limiting examples of these C_p groups are cyclopentadienyl, indenyl, 4,5,6,7-tetrahydroindenyl, fluorenyl groups and the corresponding methylsubstituted groups. However, complexes are preferred wherein the group $R'' = C_p$ has a structure included in the previous definition of A , and is more preferably equal to A .

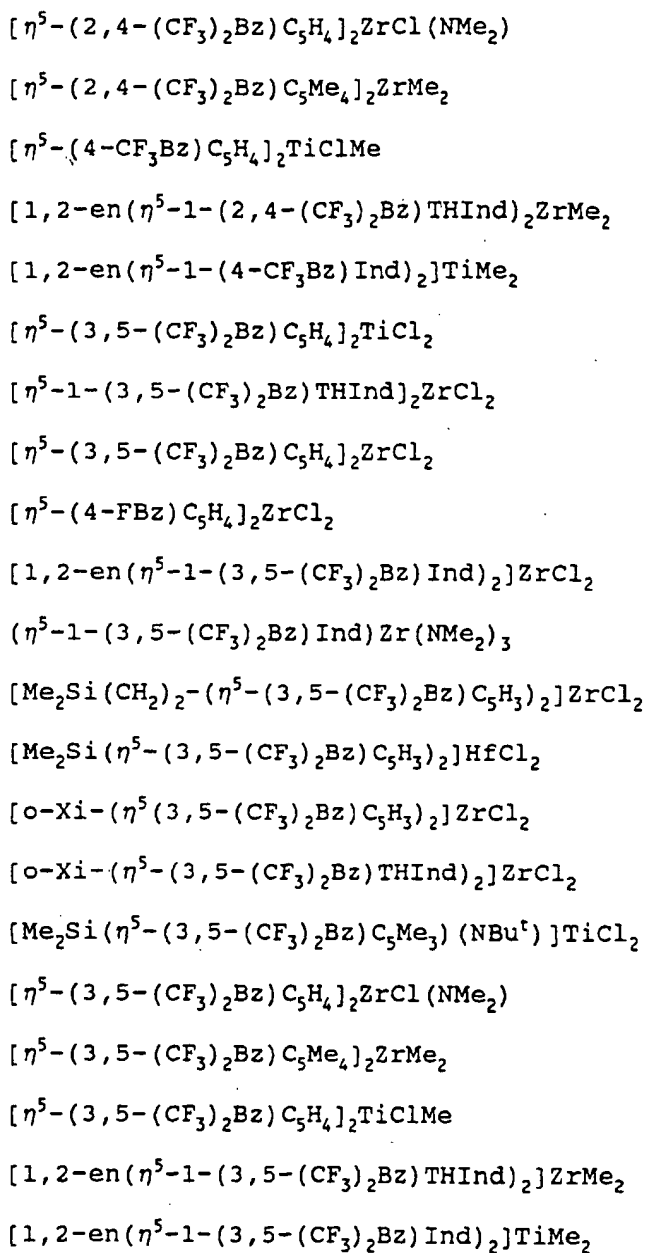
[0032] When "x" = 1, the group R'' is linked to the A group by the bridge R''' , in which case it evidently represents a group comprised in the definition of R' or, respectively, C_p , but having a position substituted by the bond with the bridge R''' . When "x" = 0, the A group and R'' group are not linked to each other.

[0033] The group R''' can be, for example, 1,2-ethylene, ethylidene, 1,3-(2-methylidene) propylene, o-phenylene, m-phenylene, o-xylidene, m-xylidene, 1,4-butylene, 2-phenyl-1,3-propylene, perfluoro-1,3-propylene, dimethylsilylene, dimethylsilylenedimethylene, dimethylgermylenedimethylene, ethylenedioxy or dimethylsilylenedioxy.

[0034] Non-limiting examples of complexes having formula (II), suitable for the purposes of the present invention, are compounds having the formulae listed in table A below.

Table A

5	=====
	$[\eta^5\text{-4-CF}_3\text{Bz)C}_5\text{H}_4]_2\text{TiCl}_2$
10	$[\eta^5\text{-1-(4-CF}_3\text{Bz)THInd}]_2\text{ZrCl}_2$
	$[\eta^5\text{-(2,4-(CF}_3)_2\text{Bz)C}_5\text{H}_4]\text{ZrCl}_2$
	$[1,2\text{-en}(\eta^5\text{-1-(2,4-(CF}_3)_2\text{Bz)Ind})_2\text{ZrCl}_2$
15	$(\eta^5\text{-1(4-CF}_3\text{Bz)Ind)Zr(NMe}_2)_3$
	$[\text{Me}_2\text{Si(CH}_2)_2\text{-(}\eta^5\text{-(4-CF}_3\text{Bz)C}_5\text{H}_3)_2]\text{ZrCl}_2$
20	$[\text{Me}_2\text{Si}(\eta^5\text{-(2,4-(CF}_3)_2\text{Bz)C}_5\text{H}_3)_2]\text{HfCl}_2$
	$[\text{o-Xi-(}\eta^5\text{-(2,4-(CF}_3)_2\text{Bz)C}_5\text{H}_3)_2]\text{ZrCl}_2$
25	$[\text{o-Xi-(}\eta^5\text{-(4-CF}_3\text{Bz)THInd})_2\text{ZrCl}_2$
	$[\text{Pr}^i(\eta^5\text{-(4-CF}_3\text{Bz)C}_5\text{H}_3)(\eta^5\text{-Flu)]ZrCl}_2$
30	$[\text{Me}_2\text{Si}(\eta^5\text{-(4-CF}_3\text{Bz)C}_5\text{Me}_3)(\text{NBu}^t)]\text{TiCl}_2$
35	
40	
45	
50	
55	



Abbreviations: o-Xi=ortho-xylylene, Me=me-

5 thyl, Bz=benzyl, Ind=indenyl, THInd=4,5,6,7-tetrahydro-

10 indenyl, Prⁱ=dimethylmethylene, Bu^t=tert-butyl, en-=1,2-

ethylidene.

=====

15 [0035] Also included in the scope of the present invention are mixtures of one or more metallocene complexes of the type previously defined. Catalysts of the present invention based on mixtures of these complexes can be advantageously used in polymerization when a wider molecular weight distribution of the polyolefins thus produced, is desired.

20 [0036] According to a particular form of embodiment, the complexes of the present invention can also be in a form supported on inert solids, preferably consisting of porous granular oxides of Si and/or Al, such as, for example, silica, alumina or silicoaluminates. Known supporting techniques can be used for the supporting of these complexes, normally comprising contact at temperatures of between room temperature and 100°C, in a suitable inert liquid medium, preferably hydrocarbon, between the carrier and complex in solution. Microspheroidal silica is particularly preferred for the supporting (average particle diameter 20-100 µm) having a BET surface area of between 150 and 700 m²/g, a total porosity > 80% and an average pore radius of between 2 and 50 nm.

25 [0037] This inert solid can be subjected to an activation process before being used as a carrier to obtain a surface with a more suitable morphology and chemical composition. During the activation process the humidity and hydroxide groups present on the surface of the inert carrier are at least partially neutralized or eliminated up to a controlled and reproducible level.

30 [0038] For example, this activation process can consist in a treatment with a solution of an alkyl derivative or an alkyl-halide of a metal selected from metals of groups 1, 2 or 13 of the Periodic Table of Elements, such as a magnesium dialkyl, a magnesium alkylchloride, an aluminium trialkyl or an aluminium alkylchloride, in a liquid aliphatic hydrocarbon solvent, such as for example, pentane, isopentane, hexane, heptane and octane. It is convenient to operate with a quantity of this alkyl derivative or alkyl-halide of between 10 and 25 parts by weight for every 100 parts by weight of granular carrier, putting the reagents in contact at a temperature of between -30 and 120°C, for times of between 0.5 and 5 hours, and preferably at a temperature of between 40 and 80°C, for times of from 1 to 2 hours. At the end of the treatment, the activated carrier is recovered, for example by filtration or decanting.

35 [0039] Alternatively, the granular carrier can be thermally activated, by heating in an inert atmosphere, to a temperature of between about 100°C and about 800°C, for a time of between 1 and 20 hours. It is preferably to operate with a carrier activated by heating in an inert atmosphere (nitrogen) to a temperature of about 600°C for a time of approximately 6 hours.

40 [0040] The preparation of the above metallocene complexes having formula (II) can be carried out with any of the known methods of organometallic chemistry, starting from a salt of the metal **M** and a cyclopentadienyl ligand having the desired structure. More generally, this ligand has the general formula (IV):



wherein "x" **A**, **R**' '' and **R**'' all have the general meaning previously specified for the complexes having formula (II).

50 [0041] For example, according to one of the above methods, the preparation of complexes having formula (II) comprises two steps, in the first of which the cyclopentadienyl binder is reacted with a lithium alkyl or lithium butyl, in an inert solvent preferably consisting of an aromatic hydrocarbon or an ether, particularly tetrahydrofuran or ethyl ether. The temperature during the reaction is preferably maintained below room temperature to avoid the creation of secondary reactions. At the end of the reaction the corresponding lithium salt of the cyclopentadienyl anion is obtained.

55 [0042] In the second step, the salt of the cyclopentadienyl anion is reacted with a salt, preferably a chloride, of the transition metal **M**, again in an inert organic solvent and at a temperature which is preferably lower than room temperature. At the end of the reaction the complex having formula (I) is separated and purified according to the known methods of organometallic chemistry.

[0043] Numerous general methods are described in literature specifically for the preparation of metallocene complexes, which basically correspond to the process described above. These methods, all well-known to experts in the field, can be generally used for the preparation of the complexes of the present invention, when the binder comprises, on at least one cyclopentadienyl ring, the particular aromatic groups with electron-attractor substituents described above. Methods of this type described in literature are, for example, those indicated in the publications of D.J.Cardin "Chemistry of Organo Zr and Hf compounds" J.Wiley and Sons Ed., New York (1986); R.Halterman "Chemical Review", vol.92 (1992) pages 965-994; R.O.Duthaler and A.Hafner "Chemical Review", vol.92 (1992) pages 807-832.

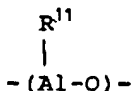
[0044] The cyclopentadienyl ligand having formula (IV), substituted with benzyl groups comprising electron-attractor groups linked to the aromatic ring, can normally be obtained with the known methods of organic synthesis. It can be synthesized, for example, by the "coupling" reaction between the cyclopentadienyl salt of an alkaline metal, preferably sodium, and a chloride of the desired benzyl group. Or an "addition" reaction can be used between an alkaline salt of a benzyl anion having the formula of the desired substituent, and a cyclopentenone to form the corresponding hydroxy-derivative which is then dehydrated to obtain the substituted cyclopentadiene.

[0045] A second object of the present invention relates to a catalyst for the (co)polymerization of α -olefins comprising the above substituted metallocene complex, or its cationic form obtained by the extraction therefrom of a non-cyclopentadienyl ligand of an anionic nature, particularly one of the R' groups of the complex having formula (II).

[0046] In a first embodiment, this catalyst of the present invention comprises, as well as the above complex, at least one co-catalyst consisting of an organo-oxygenated derivative of a metal M' selected from aluminium, gallium and tin. This can be defined as a compound in which the metal is linked to at least one oxygen atom and at least one organic R¹⁰ group, wherein R¹⁰ is C₁-C₁₀ hydrocarbyl, linear or branched. R¹⁰ is preferably a linear C₁-C₄ alkyl, even more preferably methyl.

[0047] In accordance with the present invention, the co-catalyst is preferably an aluminoxane, more preferably methylaluminoxane.

[0048] As is known, aluminoxanes are compounds containing Al-O-Al bonds, with a variable O/Al ratio, which can be obtained in the art by the reaction, under controlled conditions, of an aluminium alkyl, or aluminium alkyl halide, with water or other compounds containing controlled quantities of water available, as for example, in the case of aluminium trimethyl, with a salt hydrate, such as aluminium hexahydrate sulfate, copper pentahydrate sulfate and iron pentahydrate sulfate. The aluminoxanes preferably used for the formation of the polymerization catalyst of the present invention are oligo- or poly-meric compounds, cyclic and/or linear, characterized by the presence of repetitive units having the formula:



wherein R¹¹ is a C₁-C₄ alkyl group, preferably methyl.

[0049] Each molecule of aluminoxane preferably contains from 4 to 70 repetitive units which may not all be equal to each other, but contain different R¹¹ groups.

[0050] In addition to the above aluminoxanes, the definition of the co-catalyst of the present invention also comprises galloxanes (in which in the previous formulae, gallium is present instead of aluminium) and stannoxanes, whose use as polymerization co-catalysts of olefins in the presence of metallocene complexes is described, for example, for stannoxanes, in patents U.S. 5.128.295 and U.S. 5.258.475.

[0051] In the (co)polymerization catalysts of ethylene and α -olefins of the present invention, the metallocene complex and the co-catalyst can be used in such proportions that the atomic ratio between the metal M' and the metal M is in the range of 10 to 10000 and preferably from 200 to 5000. They are put in contact with each other with different procedures depending on the specific requirements of the polymerization process in which they are used. In particular the preparation of the polymerization catalyst of the present invention can be carried out by adding the metallocene complex to the (co)catalyst or viceversa. In addition, the mixing of the two components can be carried out with satisfactory results both before introducing the olefin to be polymerized and in the presence of said olefin.

[0052] In a second embodiment, the catalyst of the present invention is an ionic adduct in which the metallocene forms the cation, which can be obtained, for example, by the extraction reaction of a suitable group sigma-bonded to the metal M in a complex having the previous formula (II). These reactions preferably take place in an inert liquid medium, preferably hydrocarbon, and are normally carried out by putting a complex having formula (II) in contact with a suitable co-catalyst (C) consisting of a compound, or a combination of compounds, capable of activating the formation of the cationic species.

[0053] This co-catalyst is preferably selected from non-protic Lewis acids capable of extracting a sigma-bonded anionic group from this neutral metallocene complex to form a non-co-ordinating anion, and organic salts whose anion is non-co-ordinating and whose cation is capable of extracting a sigma-bound anionic group from this neutral metallocene complex to form a neutral compound. Typical examples of organic salts are the tetra(perfluoroaryl)borates of dialkylanilinium or triarylcarbenium. Typical examples of Lewis acids are tris(perfluoroaryl)-boranes or -borates.

[0054] According to a particular aspect of the present invention, when the metallocene complex does not comprise alkyl or amidic R' groups linked to the metal M, it is first interacted with a suitable alkylating agent, such as an alkyl-magnesium or an alkyl-aluminium, and subsequently combined with the co-catalyst (C) to form the catalyst of the present invention.

[0055] Examples of the above formation reactions of the cationic species are qualitatively schematized in the list below, which however does not limit the scope of the present invention:

i) by the reaction of a metallocene having the previous general formula (II), in which, preferably, at least one of the R' groups is an anion of a weak acid, more preferably alkyl, aryl or dialkylamide, with an ionic compound whose cation is capable of extracting this R' group to form a neutral compound, and whose anion is non-co-ordinating, such as, for example, triphenylcarbenium tetrakis-(pentafluorophenyl)borate or dimethylanilinium tetrakis-(pentafluorophenyl) borate;

ii) by the reaction of any non-ionic metallocene complex of the present invention, preferably having the previous formula (II), with an alkylating agent, preferably a magnesium dialkyl or an aluminium trialkyl, used in molar excess 5-50/1, followed by the reaction with a strong aprotic Lewis acid, such as, for example, tris(pentafluorophenyl) boron, in a practically stoichiometric quantity with the metal M;

iii) by the reaction of a metallocene having the previous formula (II), in which at least one R' group is alkyl or alkylene, with an almost stoichiometric quantity or in slight excess of a strong Lewis acid, such as, for example, tris(pentafluorophenyl)boron.

The above reactions, and possibly others not included in those listed above, for the formation of cationic metallocene complexes capable of polymerizing α -olefins, without the necessity of using a great excess of co-catalyst such as an aluminoxane, are generally described in literature and known to experts in the field.

[0056] As an example, for the description of suitable co-catalysts (C) and processes for the formation of cationic metallocenes, reference can be made to the publications of R.R.Jordan in "Advances in Organometallic Chemistry", vol. 32 (1990), pages 325-387, and X.Yang et al. in "Journal of the American Chemical Society", vol. 116 (1994), page 10015, as well as the following patent publications:

- European patent applications published with the Nr. EP-A 522.581, EP-A 495 375, EP-A 520732, EP-A 478913, EP-A 468651, EP-A 427697, EP-A 421659, EP-A 418044;
- International applications published with the Nr.: WO 92/00333; WO 92/05208;
- United States patents: US 5064802, US 2827446, US 5066739.

[0057] Non-limiting examples of ionic metallocene derivatives which can be used as catalysts of the present invention are listed below in table B, with reference to the respective precursors from whose combination they are obtained:

Table B

	Metalloocene	Co-Catalyst (C)
5	$[\text{o-Xi}-(\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_3)_2]\text{ZrCl}_2$	
	$[\eta^5-1-(3,5-(\text{CF}_3)_2\text{Bz})\text{THInd}]_2\text{ZrMe}_2$	$\left\{ \begin{array}{l} \text{B}(\text{C}_6\text{F}_5)_3 \\ (\text{MeNHPh})^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \\ (\text{Ph}_3\text{C})^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \end{array} \right\}$
10	$[\text{o-Xi}-(\eta^5-(4-\text{CF}_3\text{Bz})\text{C}_5\text{H}_3)_2]\text{ZrMe}_2$	
	$[\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{Me}_4]_2\text{ZrMe}_2$	
	$[\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_4]_2\text{TiClMe}$	
15	$[1,2\text{-en}(\eta^5-1-(2,4-(\text{CF}_3)_2\text{Bz})\text{THInd})_2]\text{ZrMe}_2$	
	Metalloocene	Alkylating Co-catalyst (C) agent
20	$[\eta^5-(2,4-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_4]_2\text{TiCl}_2$	
	$[\eta^5-1-(3,5-(\text{CF}_3)_2\text{Bz})\text{THInd}]_2\text{ZrCl}_2$	
	$[\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_4]_2\text{ZrCl}_2$	
25	$[1,2\text{-en}(\eta^5-1-(2,4-(\text{CF}_3)_2\text{Bz})\text{Ind})_2]\text{ZrCl}_2$	
	$[\eta^5-1-(3,5-(\text{CF}_3)_2\text{Bz})\text{Ind}]\text{Zr}(\text{NMe}_2)_3$	
	$[\text{Ph}_2\text{Si}(\eta^5-1-(2,4-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_3)_2]\text{ZrCl}_2$	$\left\{ \begin{array}{l} \text{AlBu}^i_3 \\ \text{AlEt}_3 \\ \text{AlMe}_3 \end{array} \right\} \left\{ \begin{array}{l} \text{B}(\text{C}_6\text{F}_5)_3 \\ (\text{Ph}_3\text{C})^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \\ (\text{Me}_2\text{NHPh})^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \end{array} \right\}$
30	$[\text{Me}_2\text{Si}(\eta^5-1-(2,4-(\text{CF}_3)_2\text{Bz})\text{Ind})_2]\text{HfCl}_2$	
	$[\text{o-Xi}-(\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_3)_2]\text{ZrCl}_2$	
	$[\text{o-Xi}-(\eta^5-(4-\text{CF}_3\text{Bz})\text{C}_5\text{H}_3)_2]\text{ZrCl}_2$	
	$[\text{o-Xi}-(\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{THInd})_2]\text{ZrCl}_2$	
35	$[\text{Me}_2\text{Si}(\eta^5-(2,4-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{Me}_3)(\text{NBu}^t)]\text{TiCl}_2$	
	$[\eta^5-(3,5-(\text{CF}_3)_2\text{Bz})\text{C}_5\text{H}_4]_2\text{ZrCl}(\text{NMe}_2)$	
40	Abbreviations: Ph=phenyl, o-Xi=ortho-xyllylene, Me=methyl, Et=ethyl, Bu ^t =tert-butyl, Bu ⁱ =iso-butyl, Bz=benzyl, Pr ⁱ =2,2-isopropylidene, Me ₂ Si=dimethylsilylene, Ind=indenyl, THInd=4.5.6.7-tetrahydroindenyl, 1,2-en=1,2-ethylidene,	
45	Ph ₂ Si=diphenylsilylene.	

[0058] Also included in the scope of the present invention are those catalysts comprising, as well as the metallocene complex of the present invention, in a neutral or ionic form, a solid, granular polymeric carrier, either inorganic or organic, preferably selected from inert inorganic oxides of the type previously described, more preferably selected from alumina, silica and silicoaluminates. These supported catalysts can, for example, be obtained with one of the known supporting techniques, normally comprising contact, in a suitable inert liquid medium, between the solid carrier, possibly activated as described above, and one or both of the components of the catalyst of the present invention, i.e. the metallocene complex and/or the co-catalyst. It is not necessary, for the purposes of the present invention, for both of these components to be supported, as the metallocene complex alone, preferably having formula (II), or the co-catalyst, preferably an aluminoxane, can also be present on the surface of the carrier. In the latter case the component which is not on the surface is subsequently put in contact with the supported component, at the moment when the active

catalyst for the polymerization is required.

[0059] One or more other additives can possibly be added to the catalyst of the present invention, or to the metallocene complex alone or the co-catalyst alone, before contact with the other component, to obtain a catalytic system which is suitable for satisfying specific requisites in the embodiment. In any case, these catalytic systems are also included in the scope of the present invention. Additives or components which can be included in the preparation and/or formulation of the catalyst of the present invention are inert solvents, such as, for example, aliphatic and/or aromatic hydrocarbons, aliphatic and aromatic ethers, weakly co-ordinating additives (Lewis bases) selected, for example, from ethers, tertiary amines and alcohols, halogenating agents such as silicon halides, halogenated hydrocarbons, preferably chlorinated, and similar products, and again all the other additional components normally used in the preparation of traditional homogeneous and heterogeneous catalysts of the metallocene type for the (co)polymerization of ethylene and α -olefins.

[0060] The catalysts of the present invention can be used with excellent results in basically all of the known (co) polymerization processes of α -olefins, such as, for example, processes in suspension, at low, medium or high pressure and at temperatures of between 50 and 240°C; processes in solution in an inert diluent operating at pressures of between 10 and 150 bars and temperatures of between 120 and 230°C; or in a gas phase, with temperatures generally within the range of 60 to 160°C, at pressures of between 5 and 50 bars. The polymers or copolymers thus obtained have very high average molecular weights, even if the processes used operate at a high temperature. If the molecular weight is to be regulated to a value which is lower than the maximum value obtainable, it is possible to use a chain transfer agent, such as, for example, hydrogen, as known in the art.

[0061] According to a particular aspect of the present invention, the catalyst for the (co)polymerization of α -olefins is prepared separately by contact of the metallocene complex with a suitable co-catalyst, preferably methylaluminumoxane, and subsequently introduced into the polymerization environment. The catalyst can be introduced first into the polymerization reactor, followed by the reagent mixture containing the olefin or the mixture of olefins to be polymerized, or the catalyst can be introduced into the reactor already containing the reagent mixture, or, finally, the reagent mixture and the catalyst can be contemporaneously fed into the reactor.

[0062] According to another aspect of the present invention, the catalyst is formed in situ in the polymerization reactor, for example by first introducing an aluminumoxane, subsequently the metallocene complex having formula (I), and finally feeding the olefinic monomer.

[0063] When the catalyst of the present invention is of the ionic type previously described, it is preferable to preform the catalyst, for example, using one of the above extraction reactions (i), (ii) or (iii), and introduce it subsequently into the polymerization reactor, before, after or contemporaneously with the α -olefin to be polymerized.

[0064] The catalysts of the present invention can be used with excellent results in the polymerization of ethylene to give linear polyethylene and in the copolymerization of ethylene with propylene or higher α -olefins to give copolymers with different characteristics depending on the specific polymerization conditions and the quantity and structure of the α -olefin itself. The catalyst of the present invention can also be conveniently used for the terpolymerization of ethylene, propylene and a diene to obtain vulcanizable rubbers of the EPDM type. Particularly in the case of the above copolymerization and terpolymerization processes of ethylene, the catalysts of the present invention enable the production of polymers having higher average molecular weights with respect to the traditional metallocene catalysts, under the same polymerization conditions and with the same quantity and type of comonomer inserted.

[0065] The present invention is further described in the following examples which however are purely illustrative and do not limit the scope of the invention itself.

[0066] The characterization by means of $^1\text{H-NMR}$ spectroscopy, mentioned in the following examples, was carried out on a nuclear magnetic resonance spectrometer mod. Bruker MSL-200.

[0067] The measurement of the molecular weights was carried out by Gel-Permeation chromatography (GPC). The analyses of the polyethylene (PE) samples were carried out in 1,2,4-trichlorobenzene (stabilized with Santonox) at 135°C with a WATERS 150-CV chromatograph using a Waters differential refractometer as detector.

[0068] The chromatographic separation was obtained with a set of μ Styragel HT columns (Waters) of which three with pore dimensions of 103, 104, 105 respectively, and two with pore dimensions of 106 Å, establishing a flow rate of the eluant of 1 ml/min. The data were received and processed with Maxima 820 software version 3.30 (Millipore); for the calculation of the number average molecular weight (M_n) and weight average molecular weight (M_w), the universal calibration principles were applied, selecting polystyrene standards for the calibration with molecular weights within the range of 6,500,000 - 2,000.

[0069] During the preparations described in the examples the commercial reagents listed below were used:

Methyl lithium (MeLi) 1.6 M in diethyl ether	ALDRICH
Butyl lithium (BuLi) 2.5 M in hexane	ALDRICH
Fluorobenzyl chloride	ALDRICH

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(continued)

p-trifluoromethylbenzylchloride	FLUKA
2,4-bistrifluoromethylbenzyl chloride	ALDRICH
Zirconium tetrachloride (ZrCl ₄)	FLUKA
Methylalumoxane (MAO) 1,5 M in toluene	WITCO

[0070] The reagents and/or solvents used in the following examples and not indicated above are those normally used and can be easily found on the market by any expert in the field.

Example 1: Synthesis of the complex bis- $[\eta^5$ -(4-fluorobenzyl)cyclopentadienyl]-zirconiumdichloride

1) Preparation of 4-fluorobenzylcyclopentadiene

[0071] 10 ml of a suspension at 30% by weight of metal sodium in toluene are added to a 500 ml glass flask, equipped with a cooler, drip-funnel, tap for the inlet of argon and magnetic stirring, containing 200 ml of anhydrous tetrahydrofuran (THF). 12 ml of freshly distilled cyclopentadiene are added drop-wise to the suspension, obtaining a limpid, colourless solution. The solution is then cooled to 5-10°C and 7.7 g of fluorobenzyl chloride (54 mmoles) are added. During the addition there is the formation of a precipitate of NaCl. The mixture is left under stirring for 2 hours, and 50 ml of water are then added. The mixture is then extracted with two portions of 50 ml of petroleum ether and the organic phase separated is concentrated to obtain an oily residue which is subsequently eluted on silica gel using petroleum ether as eluant. After evaporation of the eluant 3.5 g of pure product are obtained, which, after characterization by NMR spectroscopy proves to be 4-fluorobenzylcyclopentadiene (37% yield with respect to the fluorobenzyl chloride).

2) Preparation of 4-fluorobenzylcyclopentadienyl lithium

[0072] 7 g of 4-fluorobenzylcyclopentadiene (40 mmoles) and 50 ml of hexane are charged, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. The solution is cooled to 0°C and 16 ml of a 2.4M solution of butyllithium in hexane are added. The temperature is then allowed to rise to room temperature and the mixture is left under stirring for a night. A precipitate is formed which is filtered, washed twice with 10 ml of hexane and finally dried. 6.5 g of the desired salt are obtained with a yield of 90%.

3) Preparation of the complex

[0073] 0.4 g of 4-fluorobenzylcyclopentadienyl lithium (2.2 mmoles) and 20 ml of THF are introduced, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. 0.414 g of ZrCl₄(THF)₂ (1.10 mmoles) previously dissolved in 30 ml of THF are added, under stirring, to the solution thus obtained. The stirring is maintained at room temperature for 48 hours. The mixture is concentrated to solidification and toluene is added to the solid; the undissolved part is filtered away and the solution is then concentrated until the product precipitates. At the end 0.18 g of white microcrystalline solid are obtained which, after characterization by NMR spectroscopy, proves to be bis- $[\eta^5$ -(4-fluorobenzyl)-cyclopentadienyl]zirconiumdichloride, with a yield of 29%.

¹H-NMR spectrum (toluene D⁸, ppm rel.to TMS): 6.85-6.72 (m); 6.1 (q,1H); 5.72 (q,1H); 5.48 (q,1H); 3.9 (d,2H).

Example 2: Synthesis of bis- $[\eta^5$ -(4-trifluoromethylbenzyl)cyclopentadienyl]-zirconiumdichloride

1) Preparation of 4-trifluoromethylbenzylcyclopentadiene

[0074] Exactly the same procedure is used as described in paragraph 1 of example 1 above, with the only difference that 10.5 g of p-trifluoromethylbenzylchloride (54 mmoles) are used instead of 7.7 g of fluorobenzyl chloride. At the end 5.1 g of pure product are obtained which, after characterization with NMR spectroscopy, proves to be 4-trifluoromethylbenzylcyclopentadiene (yield 42% with respect to the initial trifluoromethylcyclopentadiene).

2) Preparation of 4-trifluoromethylbenzylcyclopentadienyl lithium

[0075] 2.5 g of 4-trifluoromethylbenzylcyclopentadiene (10 mmoles) and 30 ml of hexane are charged, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. The same procedure is then carried out as in paragraph 2 of example 1 above, using 4.5 ml of a 2.5 M solution of butyllithium in hexane. At the end, 2.1 g of the

desired salt are obtained with a yield of 80%.

3) Preparation of the complex

5 [0076] 0.75 g of 4-trifluoromethylbenzylcyclopentadienyl lithium (2.6 mmoles) and 30 ml of THF are introduced, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. 0.414 g of $ZrCl_4(THF)_2$ previously dissolved in 30 ml of THF are added, under stirring, to the solution thus obtained. The same procedure is then carried out as in paragraph 3 of example 1 above, obtaining at the end 0.512 g of white microcrystalline solid which after

10 characterization by NMR spectroscopy proves to be bis- $[\eta^5\text{-}(4\text{-trifluoromethylbenzyl})\text{cyclopentadienyl}]\text{-zirconium-dichloride}$, with a yield of 61%.

$^1\text{H-NMR}$ spectrum (toluene D^8 , ppm rel. to TMS): 7.2-6.8 (m); 5.82 (t, 2H); 5.6 (t, 2H); 3.95 (s, 2H).

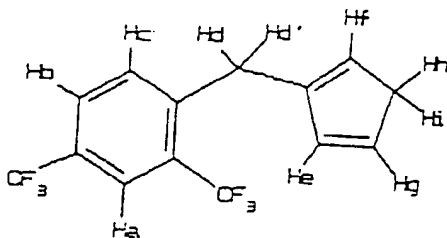
Example 3: Synthesis of bis- $[\eta^5\text{-}(2,4\text{-bistrifluoromethyl benzyl})\text{cyclopentadienyl}]\text{-zirconiumdichloride}$

15 1) Preparation of 2,4-bistrifluoromethylbenzylcyclopentadiene

[0077] 7 ml of a suspension at 30% by weight of metal sodium in toluene are added to a 500 ml glass flask, containing 100 ml of anhydrous tetrahydrofuran (THF). 9 ml of freshly distilled cyclopentadiene are added drop-wise to the suspension, maintained at a temperature lower than 30°C , obtaining a colourless solution.

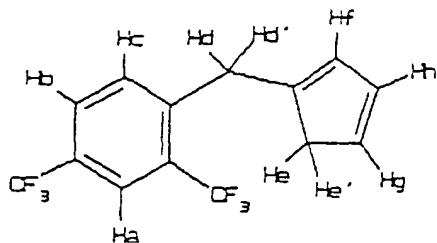
20 [0078] The solution is then cooled to 0°C and 20 g of 2,4-bistrifluoromethylbenzyl chloride (76 mmoles) are added. The temperature is left to rise to room temperature and the mixture is left under stirring for about 4 hours until the chloride disappears. 50 ml of water are then added, and the mixture is then extracted with two portions of 50 ml of petroleum ether. The organic phase separated is concentrated to obtain an oily yellow-coloured residue (21 g), containing a mixture of cyclopentadiene mono- and di-substituted with the benzyl group. This residue is immediately distilled, collecting the fraction with a boiling point of 40°C at 13.1 Pa. The product thus obtained (3.5 g, yield 14%) must be maintained in a solution of hexane at a temperature of 0°C or less, to avoid dimerization, and it proved to consist

25 of two isomers having the structures (V) and (VI) below, of which the $^1\text{H-NMR}$ characterization is given



(V)

40 $^1\text{H-NMR}$ spectrum (CDCl_3 , ppm rel. to TMS): 7.85 (s, Ha); 7.26 (d, Hb, $J=8.12$ Hz); 6.99(6.89) (d, Hc, $J=8.12$ Hz); 5.95(5.76) (dq, He, $J_{\text{Hg-He}}=4.56$ Hz, $J_{\text{He-Hh}}=2.66$ Hz, $J_{\text{He-Hi}}=1.36$ Hz).



(VI)

55 $^1\text{H-NMR}$ spectrum (CDCl_3 , ppm rel. to TMS): 7.85 (s, Ha); 7.26 (d, Hb, $J=8.12$ Hz); 6.99(6.89) (d, Hc, $J=8.12$ Hz); 5.95(5.76) (dq, Hg, $J_{\text{Hg-Hh}}=4.56$ Hz, $J_{\text{Hg-He}}=2.66$ Hz, $J_{\text{Hg-He}}=1.36$ Hz).

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2) Preparation of 2,4-bistrifluoromethylbenzylcyclopentadienyl lithium

[0079] 3.5 g of 2,4-bistrifluoromethylbenzylcyclopentadiene and 30 ml of hexane are charged, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. 6 ml of a 2.5 M solution of butyllithium in hexane are then added. There is an immediate reaction with the development of heat and the formation of a yellow precipitate which is washed several times with hexane by decanting and finally dried. 3.0 g of the desired salt are obtained with a yield of 85%.

3) Preparation of the complex

[0080] 1.0 g of 2,4-bistrifluoromethylbenzylcyclopentadienyl lithium (3.36 mmoles) in 40 ml of THF are introduced, in an argon atmosphere, into a tailed test-tube equipped with magnetic stirring. 0.60 g of $ZrCl_4(THF)_2$ (1.59 mmoles) are added, under stirring at 0°C, to the solution. The mixture is then left at room temperature for 8 hours. The solvent is evaporated under vacuum and the residue is extracted with 30 ml of toluene. The toluene phase is concentrated to about 15 ml, 3-4 ml of hexane are added and the mixture is left to rest. A crystalline solid is formed which after filtration and drying, has a weight of 0.7 g. The product after characterization by NMR spectroscopy, proves to be bis- $[\eta^5$ -(2,4-bistrifluoromethylbenzyl)-cyclopentadienyl]zirconiumdichloride, with a yield of 63%.

1H -NMR spectrum (benzene D^6 , ppm rel.to TMS): 7.75 (s, 2H); 7.20 (d, 1H); 7.05 (d, 1H); 5.85 (t, 2H); 5.52 (t, 2H); 4.22 (s, 2H).

Examples 4-6: polymerization of ethylene

[0081] Various polymerization tests of ethylene were carried out corresponding to examples 4 to 6, using the following general procedure.

[0082] 500 ml of toluene (previously distilled on metal sodium) and 0.54 ml of the above solution of MAO at 10% in toluene are charged into a BUCHI autoclave with a glass reactor having a volume of 1 litre, equipped with a propeller stirrer, thermocouple and heating jacket connected to a thermostat for the temperature control, maintained under vacuum for at least two hours interrupted by three washings with nitrogen. The pressure-resistant reactor is heated to 70°C and the desired quantity of metallocene complex according to the present invention is introduced, with a syringe, so that the atomic ratio between the aluminum introduced as MAO and the transition metal (in this case zirconium) in the complex and the aluminium is equal to about 2500. The pressure-resistant reactor is pressurized with ethylene up to a pressure of 0.2 MPa (2 atms), and the polymerization is carried out for 30 minutes, continuously feeding the ethylene to maintain the pressure constant for the whole duration of the test. The polymer is recovered by precipitation in acidified methanol and subsequent washings with acetone. The polymer thus obtained is linear polyethylene (HDPE) which is characterized by measuring the number average molecular weight (M_n) and the weight average molecular weight (M_w) and the molecular weight distribution ($MHD=M_w/M_n$).

[0083] Different polymerization tests were carried out with the above procedure, using the complexes prepared according to the previous examples 1 to 5. The conditions and results of the polymerizations are summarized in Table 1, below, in which, for each example, the zirconium complex is identified in the second column with reference to the respective preparation example.

Example 7 (comparative)

[0084] For comparative purposes a polymerization test of ethylene was carried out under the same conditions as the previous examples 5 to 8, but using bis- $(\eta^5$ -cyclopentadienyl) zirconium dichloride $(\eta^5-C_5H_5)_2ZrCl_2$ as metallocene complex. The results and characterization of the polyethylene thus obtained are shown in table 1.

TABLE 4: Ethylene polymerization

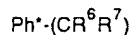
Example Nr.	Zirconium complex			Yield (PE g)	Activity (g _{PE} /mg _{Zr} *hr)	Mn	MWD
	Reference example Nr	Quantity (mg)	Concentration (moles*10 ⁶)				
4	1	0.17	0.70	7.4	354	190,000	2.4
5	3	0.25	0.70	1.3	62	398,000	n.m.
6 (a)	3	0.40	1.10	5.8	220	311,000	n.m.
7	(η^5 -C ₅ H ₅)ZrCl ₂	0.10	0.70	6.9	326	142,000	2.3

(a) Ethylene pressure = 1.0 MPa (10 Atm)

n.m. = Not measured

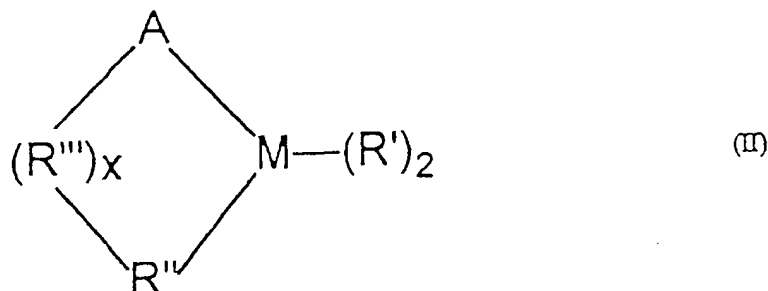
Claims

1. Metallocene complex of a metal M selected from titanium, zirconium and hafnium, comprising at least one anionic group A containing a η^5 -cyclopentadienyl ring coordinated to the metal M, characterized in that the said anionic group is substituted in at least one position of the cyclopentadienyl ring with a radical having the formula:



wherein: R^6 and R^7 are independently hydrogen, halogen, or a C_1 - C_4 alkyl group, Ph^* is a C_6 - C_{14} group comprising an aromatic ring linked to the $-\text{CR}^6\text{R}^7-$ and substituted with at least one, and up to a maximum of three, electron-attractor groups selected from fluorine, halogenated hydrocarbon radicals having from 1 to 15 carbon atoms, halogenated alkylsilyl radicals having from 1 to 15 carbon atoms, alkoxy-carbonyl radicals, halogenated or non-halogenated, having from 2 to 15 carbon atoms and alkoxy- or arylalkoxy-alkyl radicals having from 2 to 15 carbon atoms.

2. Metallocene complex according to claim 1, which can be represented with the following formula (II):



wherein:

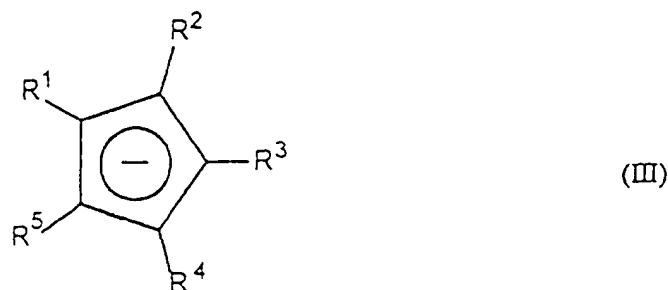
M represents a metal selected from titanium, zirconium or hafnium;

each of the two **R'** independently represents a substituent group selected from hydride, halide, a C_1 - C_8 alkyl group, a C_3 - C_{12} alkylsilyl group, a C_5 - C_8 cycloalkyl group, a C_6 - C_{10} aryl group, a C_1 - C_8 alkoxy group, a C_1 - C_8 carboxyl group, a C_2 - C_{10} dialkylamide group and a C_4 - C_{20} alkylsilylamide group;

R'' represents a substituent group of the same kind as the previous **R'** groups, independently selected from these, or a second anion containing an η^5 -cyclopentadienyl ring substituted or non-substituted, co-ordinated to the metal **M**, possibly selected from the substituted cyclopentadienyl anions included in the following definition of **A**;

R''' represents a divalent group having from 1 to 10 carbon atoms, possibly containing one or more heteroatoms, preferably O, N, P, Sn, Ge or Si, which is bridge-linked between **A** and **R''** with covalent bonds,

A is an anion containing a substituted η^5 -cyclopentadienyl ring, co-ordinated to the metal **M**, represented by the following formula (III):

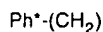


15 wherein:

each R^i group (with $i = 1, 2, 3, 4$ or 5) can be independently hydrogen, halogen, a C_1 - C_8 alkyl group, a C_3 - C_{12} alkylsilyl group, a C_5 - C_8 cycloalkyl group, a C_6 - C_{14} aryl group, a C_6 - C_{15} arylalkyl group, a C_1 - C_8 alkoxy group, a C_1 - C_8 carboxyl group, or two R^i adjacent groups can combine with each other to form a cyclic aliphatic or aromatic structure comprising at least three, and preferably from 5 to 8 non-metallic atoms different from hydrogen and halogen; and

"x" can be 0 or 1, on the condition that when "x" is 1, the divalent R^x group is linked on one side to the **A** group as a substitute of one of the R^i groups having formula (III), and on the other side to the R^* group, as a substitute for any of its hydrogen atoms;

25 characterized in that at least one R^i in formula (III) of the **A** group, and possibly also in the formula of the R^* group, when this is represented by formula (III), consists of a radical having the formula:



wherein: Ph^* is defined as in claim 1 above.

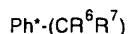
- 35
3. Metallocene complex according to any of the previous claims, wherein the electron-attractor group on Ph^* is selected from fluorinated hydrocarbon radicals, having from 1 to 15 carbon atoms, and fluorinated alkylsilyl radicals, having from 1 to 15 carbon atoms, in which at least fluorine atom is linked to a carbon atom or to a silicon atom in position 1 or 2 with respect to the aromatic ring of the Ph^* group.
 - 40 4. Metallocene complex according to any of the previous claims from 2 to 3, wherein **A** is an η^5 -cyclopentadiene anion having formula (III) wherein R^1 is a $Ph^* -CH_2$ - group defined as in claim 2 above, particularly bis(fluoroalkyl) benzyl, and each of the remaining R^2 , R^3 , R^4 and R^5 are independently hydrogen or methyl.
 5. Metallocene complex according to any of the previous claims from 2 to 4, wherein R^* in formula (II) is a C_p group containing an η^5 -cyclopentadienyl ring co-ordinated to the metal **M**.
 - 45 6. Metallocene complex according to claim 5, wherein the C_p group has a structure included in the previous definition **A** in formula (III) of claim 2, and is more preferably equal to **A**.
 7. Metallocene complex according to claim 6, selected from:

50 bis- $[\eta^5$ -(4-fluorobenzyl) cyclopentadienyl] zirconiumdichloride;
 bis- $[\eta^5$ -(4-trifluoromethylbenzyl)cyclopentadienyl] zirconiumdichloride
 bis- $[\eta^5$ -(2,4-bistrifluoromethylbenzyl)cyclopentadienyl]zirconiumdichloride
 - 55 8. Catalyst for the (co)polymerization of ethylene and/or α -olefins comprising at least one metallocene complex according to any of the previous claims, and at least one co-catalyst.
 9. Catalyst according to claim 8, wherein the metallocene complex is a complex having formula (II) in claim 2 above.

10. Catalyst according to claim 8 or 9, wherein the co-catalyst consists of an organo-oxygenated derivative of a metal **M'** selected from aluminium, gallium and tin.
- 5 11. Catalyst according to claim 10, wherein the organo-oxygenated derivative of **M'** is an aluminoxane, preferably methylaluminoxane.
12. Catalyst according to claim 10 or 11, wherein the atomic ratio between the metal **M'**, in the co-catalyst and the metal **M**, in the metallocene complex, is comprised between 10 and 10000, preferably between 200 and 5000.
- 10 13. Catalyst according to any of the previous claims 8 and 9, comprising a cationic metallocene complex, characterized in that this cationic metallocene complex is obtained from the combination of a neutral metallocene complex according to any of the previous claims from 1 to 7 with a co-catalyst capable of extracting a sigma-bound anionic group therefrom.
- 15 14. Catalyst according to claim 13, wherein the co-catalyst is selected from non-protic Lewis acids capable of extracting a sigma-bonded anionic group from the neutral metallocene complex to form a non-co-ordinating anion, and organic salts whose anion is non-co-ordinating and whose cation is capable of extracting a sigma-bonded anionic group from this neutral metallocene complex to form a neutral compound.
- 20 15. Catalyst according to claim 13 or 14, wherein the neutral metallocene complex comprises at least one alkyl or amide group linked to the metal **M**.
16. Catalyst according to any of the previous claims from 8 to 15, characterized in that at least one component selected from the metallocene complex and the co-catalyst is supported on a polymeric, inorganic or organic solid granular carrier.
- 25 17. Catalyst according to claim 16, wherein the solid granular carrier is selected from alumina, silica and silicoaluminates.
- 30 18. Process for the (co)polymerization of alpha-olefins, comprising feeding at least one alphaolefin and optional comonomers to a continuous or batch reactor, and (co)polymerizing the mixture in suspension or solution in a suitable liquid medium, or in gas phase, in the presence of a polymerization catalyst, characterized in that said catalyst is the catalyst according to any of the previous claims from 8 to 17.
- 35 19. Process according to claim 18, wherein the alpha-olefin is ethylene.
20. Process according to any of the previous claims 18 or 19, wherein the catalyst is formed in situ in the polymerization reactor by contact of the metallocene complex according to any of the previous claims from 1 to 7, with a co-catalyst consisting of an organo-oxygenated derivative of aluminium, preferably an aluminoxane.
- 40

Patentansprüche

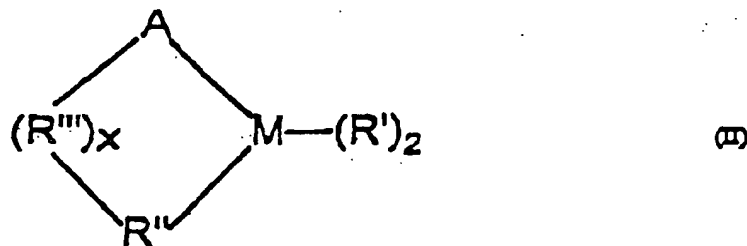
- 45 1. Metallocenkomplex eines Metalles **M**, ausgewählt aus Titan, Zirkon und Hafnium, umfassend mindestens eine anionische Gruppe **A**, welche einen η^5 -Cyclopentadienylring mit dem Metallatom **M** koordiniert enthält, dadurch gekennzeichnet, daß die anionische Gruppe an mindestens einer Position des Cyclopentadienyl-Rings mit einem Radikal substituiert ist, welches die Formel aufweist:



worin: R^6 und R^7 unabhängig voneinander Wasserstoff, Halogen oder eine C_1 - C_4 Alkylgruppe repräsentieren, worin Ph^{\cdot} eine C_6 - C_{14} -Gruppe ist, welche einen aromatischen Ring umfasst, der an die CR^6R^7 -Gruppe gebunden ist und welcher mit mindestens einer bis zu einem Maximum von drei Elektronen anziehenden Gruppen substituiert ist, welche ausgewählt sind aus Fluor, halogenierten Kohlenwasserstoffradikalen mit einem bis 15 Kohlenstoffatomen, halogenierten Alkylsilyl-Radikalen mit einem bis 15 Kohlenstoffatomen, Alkoxy-Alkylradikalen, welche halogeniert oder nicht-halogeniert sind und 2 bis 15 Kohlenstoffatome enthalten, und Alkoxy- oder Arylalkoxy-Alkylradikale mit 2 bis 15 Kohlenstoffatomen.

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2. Metallocenkomplex nach Anspruch 1, welcher durch die folgende Formel (II) darstellbar ist:



15 worin:

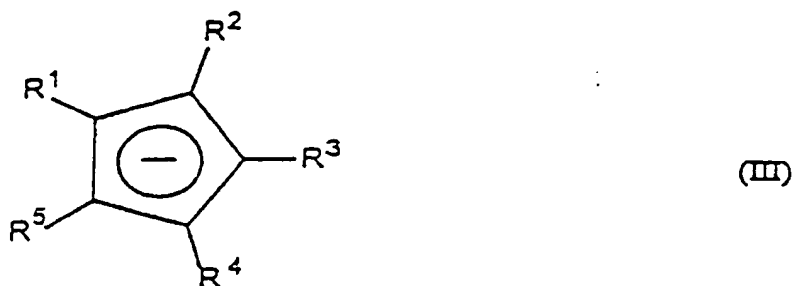
M ein Metall repräsentiert, ausgewählt aus Titan, Zirkon oder Hafnium;

20 jeder der beiden R¹-Reste unabhängig von dem anderen eine Substituenten-Gruppe repräsentiert, welche ausgewählt ist aus Hydrid, Halogen, einer C₁-C₈-Alkylgruppe, einer C₃-C₁₂-Alkyl-Silylgruppe, einer C₅-C₈-Cyclo-Alkylgruppe, einer C₆-C₁₀-Arylgruppe, einer C₁-C₈-Alkoxygruppe, einer C₁-C₈-Carboxylgruppe, einer C₂-C₁₀-Dialkylamidgruppe und einer C₆-C₂₀-Alkylsilylamidgruppe;

25 R'' eine Substituentengruppe derselben Art wie die vorherigen R¹-Gruppen, unabhängig von diesen ausgewählt, oder ein zweites Anion repräsentiert, welches einen substituierten oder unsubstituierten η⁵-Cyclopentadienyl-Ring enthält, welcher mit dem Metall M koordiniert ist, und welches ausgewählt sein kann, aus den substituierten Cyclopentadienyl-Anionen, welche in der folgenden Definition von A aufgeführt sind;

30 R''' eine divalente Gruppe mit 1 bis 10 Kohlenstoffatomen repräsentiert, welche eines oder mehrere Heteroatome enthalten kann, vorzugsweise O, N, P, Sn, Ge oder Si, und welche in der Art einer Brücke zwischen A und R'' an diese mit kovalenten Bindungen gebunden ist,

35 A ein Anion darstellt, welches einen substituierten η⁵-Cyclopentadienyl-Ring enthält, welcher mit dem Metall M koordiniert ist und welcher durch die folgende Formel (III) repräsentiert wird:

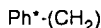


50 worin: jede Rᵀ-Gruppe (worin i = 1, 2, 3, 4 oder 5 ist) unabhängig voneinander Wasserstoff, Halogen eine C₁-C₈ Alkylgruppe, eine C₃-C₁₂ Alkylsilylgruppe, eine C₅-C₈ Cycloalkylgruppe, eine C₆-C₁₄ Arylgruppe, eine C₆-C₁₅ Arylalkylgruppe, eine C₁-C₈ Alkoxygruppe, eine C₁-C₈-Carboxylgruppe darstellen, oder zwei benachbarte Rᵀ-Gruppen miteinander kombiniert sein können, um eine zyklische, aliphatische oder aromatische Struktur zu bilden, welche mindestens drei und bevorzugt 5 bis 8 nicht-metallische Atome, welche verschieden von Wasserstoff und Halogen sind, umfassen; und

55 worin: "x" 0 oder 1 sein kann, unter der Bedingung, daß wenn "x" gleich 1 ist, die divalente R'''-Gruppe mit einer Seite an die A-Gruppe gebunden ist, als ein Substitut für eine der Rᵀ-Gruppen mit der Formel (III) und auf der anderen Seite mit der R'' Gruppe verbunden ist als ein Substitut für irgendeines seiner Wasserstoffa-

tome;

dadurch gekennzeichnet, daß mindestens die Rⁱ-Reste in der Formel (III) der A-Gruppe, und möglicherweise ebenfalls in der Formel der Rⁿ-Gruppen, wenn diese durch die Formel (III) repräsentiert sind, aus einem Radikal mit der Formel bestehen:



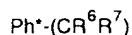
worin Ph* wie in Anspruch 1 definiert ist.

3. Metallocenkomplex nach einem der voranstehenden Ansprüche, worin die elektronenanziehende Gruppe an der Ph^{*}-Gruppe ausgewählt ist aus fluorierten Kohlenwasserstoffradikalen mit 1 bis 15 Kohlenstoffatomen und fluorierten Alkylsilylradikalen mit 1 bis 15 Kohlenstoffatomen, bei denen mindestens ein Fluoratom mit einem Kohlenstoffatom oder einem Siliciumatom in der Position 1 oder 2 bezüglich des aromatischen Rings der Ph^{*}-Gruppe verbunden ist.
4. Metallocenkomplex nach einem der voranstehenden Ansprüche 2 bis 3 worin A ein η⁵-Cyclopentadien-Anion der Formel (III) ist, worin R¹ eine Ph^{*}-CH₂-Gruppe wie in Anspruch 2 definiert ist, insbesondere bis(Fluoroalkyl)-benzyl, und jeder der verbleibenden R², R³, R⁴ und R⁵-Reste unabhängig voneinander Wasserstoff oder Methyl sind.
5. Metallocenkomplex nach einem der voranstehenden Ansprüche 2 bis 4, worin Rⁿ in der Formel (II) eine c_p-Gruppe ist, welche einen η⁵-Cyclopentadienyl-Ring koordiniert mit dem Metall M enthält.
6. Metallocenkomplex nach Anspruch 5, worin die c_p-Gruppe eine Struktur aufweist, welche unter die vorhergehende Definition A der Formel (III) von Anspruch 2 fällt und weiter bevorzugt gleich A ist.
7. Metallocenkomplex nach Anspruch 6, ausgewählt aus:
 - bis-(η⁵-(4-Fluorobenzyl)-cyclopentadienyl)-zirconiumdichlorid
 - bis-(η⁵-(4-Trifluoromethylbenzyl)-cyclopentadienyl)-zirconiumdichlorid
 - bis-(η⁵-(2,4-Bistrifluoromethylbenzyl)-cyclopentadienyl)zirconiumdichlorid.
8. Katalysator für die (Co-)Polymerisation von Ethylen und/oder α-Olefinen, umfassend mindestens einen Metallocenkomplex nach einem der voranstehenden Ansprüche und mindestens einen Co-Katalysator.
9. Katalysator nach Anspruch 8, worin der Metallocenkomplex ein Komplex der Formel (II) in Anspruch 2 ist.
10. Katalysator nach Anspruch 8 oder 9, worin der Co-Katalysator, aus einem organo-oxidierten Derivat eines Metalles M' besteht, ausgewählt aus Aluminium, Gallium und Zinn.
11. Katalysator nach Anspruch 10, worin das organo-oxidierte Derivat von M' ein Aluminoxan, vorzugsweise Methylaluminoxan ist.
12. Katalysator nach Anspruch 10 oder 11, worin das Atomverhältnis zwischen dem Metall M' in dem Co-Katalysator und dem Metall M in dem Metallocenkomplex zwischen 10 und 10 000, vorzugsweise zwischen 200 und 5000 liegt.
13. Katalysator nach einem der voranstehenden Ansprüche 8 und 9, umfassend einen kationischen Metallocenkomplex, dadurch gekennzeichnet, daß dieser kationische Metallocenkomplex aus einer Kombination eines neutralen Metallocenkomplexes nach einem der voranstehenden Ansprüche 1 bis 7 mit einem Co-Katalysator erhalten wird, welcher in der Lage ist, aus diesem eine sigma-gebundene anionische Gruppe hieraus zu abstrahieren.
14. Katalysator nach Anspruch 13, worin der Co-Katalysator ausgewählt ist aus nicht-protischen Lewissäuren, welche in der Lage sind, eine sigma-gebundene anionische Gruppe aus dem neutralen Metallocenkomplex zu abstrahieren, um ein nicht-koordinierendes Anion zu bilden, und organischen Salzen, deren Anion nicht-koordinierend ist und deren Kation in der Lage ist, eine sigma-gebundene anionische Gruppe aus diesem neutralen Metallocenkomplex zu abstrahieren, um eine neutrale Verbindung zu bilden.

15. Katalysator nach Anspruch 13 oder 14, worin der neutrale Metallocenkomplex mindestens eine Alkyl- oder Amidgruppe umfasst, welche an das Metall M gebunden ist.
16. Katalysator nach einem der voranstehenden Ansprüche 8 bis 15, dadurch gekennzeichnet, daß mindestens der Metallocenkomplex und/oder der Co-Katalysator auf einem polymeren, anorganischen oder organischen festen granularen Träger aufgebracht ist.
17. Katalysator nach Anspruch 16, worin der feste granuläre Träger ausgewählt ist, aus Aluminiumoxid, Siliciumoxid und Siliciumaluminaten.
18. Verfahren für die (Co-)Polymerisation von α -Olefinen, umfassend das Zuführen von mindestens einem α -Olefin und gegebenenfalls Co-Monomeren zu einem kontinuierlichen oder Chargenreaktor, und (Co-)polymerisieren der Mischung in Suspension oder Lösung in einem geeigneten flüssigen Medium oder in Gasphase in Gegenwart eines Polymerisationskatalysators, dadurch gekennzeichnet, daß der Katalysator ein Katalysator nach einem der vorangehenden Ansprüche 8 bis 17 ist.
19. Verfahren nach Anspruch 18, worin das α -Olefin, Ethylen ist.
20. Verfahren nach einem der voranstehenden Ansprüche 18 oder 19, worin der Katalysator in situ in dem Polymerisationsreaktor durch In-Kontakt-bringen des Metallocenkomplexes nach einem der voranstehenden Ansprüche 1 bis 7, mit einem Co-Katalysator gebildet wird, welcher aus einem organo-oxidierten Derivat von Aluminium, vorzugsweise einem Aluminoxan besteht.

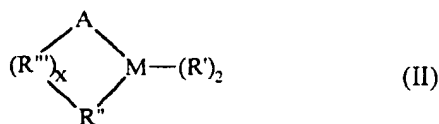
Revendications

1. Complexe de type métallocène d'un métal M choisi parmi le titane, le zirconium et l'hafnium, comprenant au moins un groupe anionique A contenant un cycle η^5 -cyclopentadiényle coordonné au métal M, caractérisé en ce que ledit groupe anionique est substitué à au moins une position du cycle cyclopentadiényle par un radical ayant la formule:



dans laquelle R^6 et R^7 sont indépendamment un atome d'hydrogène ou d'halogène ou un groupe alkyle en C_1 - C_4 , Ph^* est un groupe en C_6 - C_{14} comprenant un cycle aromatique lié au groupe $-\text{CR}^6\text{R}^7$ - et substitué par au moins un et jusqu'à un maximum de trois groupes attracteurs d'électrons choisis parmi le fluor, des radicaux hydrocarbonés halogénés de 1 à 15 atomes de carbone, des radicaux alkylsilyle halogénés de 1 à 15 atomes de carbone, des radicaux alcoxycarbonyle halogénés ou non halogénés de 2 à 15 atomes de carbone et des radicaux alcoxyalkyle ou arylalcoxyalkyle de 2 à 15 atomes de carbone.

2. Complexe de type métallocène selon la revendication 1, qui peut être représenté par la formule (II) suivante:



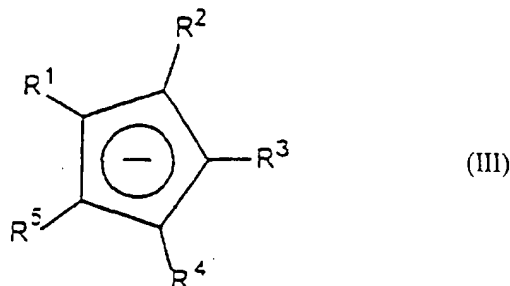
dans laquelle:

M représente un métal choisi parmi le titane, le zirconium ou l'hafnium;
 chacun des deux R' représente indépendamment un groupe substituant choisi parmi un hydrure, un halogénure, un groupe alkyle en C_1 - C_8 , un groupe alkylsilyle en C_3 - C_{12} , un groupe cycloalkyle en C_5 - C_8 , un groupe aryle en C_6 - C_{10} , un groupe alcoyle en C_1 - C_8 , un groupe carboxyle en C_1 - C_8 , un groupe dialkylamide en C_2 - C_{10} et un groupe alkylsilylamide en C_4 - C_{20} ;
 R'' représente un groupe substituant du même type que les groupes R' précédents, choisi indépendamment

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parmi ces derniers, ou un second anion contenant un cycle η^5 -cyclopentadiényle substitué ou non substitué, coordonné au métal M, pouvant être choisi parmi les anions cyclopentadiényle substitués compris dans la définition de A ci-dessous;

Rⁱⁱⁱ représente un groupe divalent de 1 à 10 atomes de carbone, pouvant contenir un ou plusieurs hétéroatomes, de préférence O, N, P, Sn, Ge ou Si, qui est lié en formant un pont entre A et Rⁱⁱ par des liaisons covalentes, A est un anion contenant un cycle η^5 -cyclopentadiényle substitué, coordonné au métal M, représenté par la formule (III) ci-dessous:

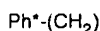


dans laquelle:

chaque groupe Rⁱ (avec i = 1, 2, 3, 4 ou 5) peut être indépendamment un atome d'hydrogène ou d'halogène, un groupe alkyle en C₁-C₈, un groupe alkylsilyle en C₃-C₁₂, un groupe cycloalkyle en C₅-C₈, un groupe aryle en C₆-C₁₄, un groupe arylalkyle en C₆-C₁₅, un groupe alcoyle en C₁-C₈, un groupe carboxyle en C₁-C₈, ou deux groupes Rⁱ adjacents peuvent se combiner entre eux pour former une structure cyclique aliphatique ou aromatique comprenant au moins 3, et de préférence de 5 à 8 atomes non métalliques différents de l'hydrogène et des halogènes; et

"x" peut être 0 ou 1, à condition que, lorsque "x" est 1, le groupe divalent Rⁱⁱⁱ soit lié d'un côté au groupe A à la place de l'un des groupes Rⁱ de la formule (III), et de l'autre côté au groupe Rⁱⁱ à la place d'un quelconque de ses atomes d'hydrogène;

caractérisé en ce qu'au moins l'un des Rⁱ de la formule (III) du groupe A, et éventuellement aussi dans la formule du groupe Rⁱⁱ lorsque celui-ci est représenté par la formule (III), est constitué d'un radical ayant la formule:



dans laquelle Ph[·] a la définition donnée dans la revendication 1.

3. Complexe de type métallocène selon l'une quelconque des revendications précédentes, dans lequel le groupe attracteur d'électrons situé sur Ph[·] est choisi parmi des radicaux hydrocarbonés fluorés de 1 à 15 atomes de carbone et des radicaux alkylsilyle fluorés de 1 à 15 atomes de carbone, dans lesquels au moins un atome de fluor est lié à un atome de carbone ou à un atome de silicium en position 1 ou 2 par rapport au cycle aromatique du groupe Ph[·].
4. Complexe de type métallocène selon l'une quelconque des revendications 2 à 3 précédentes, dans lequel A est un anion η^5 -cyclopentadiène de formule (III) dans laquelle R¹ est un groupe Ph[·]-CH₂- ayant la définition donnée dans la revendication 2 ci-dessus, en particulier un groupe bis(fluoroalkyl)benzyle, et chacun des R², R³, R⁴ et R⁵ restants est indépendamment un atome d'hydrogène ou un groupe méthyle.
5. Complexe de type métallocène selon l'une quelconque des revendications 2 à 4 précédentes, dans lequel Rⁱⁱ, dans la formule (II), est un groupe C_p contenant un cycle η^5 -cyclopentadiényle coordonné au métal M.
6. Complexe de type métallocène selon la revendication 5, dans lequel le groupe C_p a une structure comprise dans la définition précédente de A dans la formule (III) de la revendication 2, et est de préférence égal à A.

7. Complexe de type métallocène selon la revendication 6, choisi parmi:
- le dichlorure de bis[η^5 -(4-fluorobenzyl)cyclopentadiényl]zirconium;
le dichlorure de bis[η^5 -(4-trifluorométhylbenzyl)cyclopentadiényl]zirconium;
5 le dichlorure de bis[η^5 -(2,4-bistrifluorométhylbenzyl)cyclopentadiényl]zirconium.
8. Catalyseur pour la (co)polymérisation d'éthylène et/ou d' α -oléfines, comprenant au moins un complexe de type métallocène selon l'une quelconque des revendications précédentes, et au moins un cocatalyseur.
- 10 9. Catalyseur selon la revendication 8, dans lequel le complexe de type métallocène est un complexe ayant la formule (II) de la revendication 2 ci-dessus.
10. Catalyseur selon la revendication 8 ou 9, dans lequel le cocatalyseur est constitué d'un dérivé organo-oxygéné d'un métal M' choisi parmi l'aluminium, le gallium et l'étain.
- 15 11. Catalyseur selon la revendication 10, dans lequel le dérivé organo-oxygéné de M' est un aluminoxane, de préférence un méthylaluminoxane.
12. Catalyseur selon la revendication 10 ou 11, dans lequel le rapport atomique entre le métal M', dans le cocatalyseur, et le métal M, dans le complexe de type métallocène, est compris entre 10 et 10 000, de préférence entre 200 et 5 000.
- 20 13. Catalyseur selon l'une quelconque des revendications 8 et 9 précédentes, comprenant un complexe de type métallocène cationique, caractérisé en ce que ce complexe de type métallocène cationique est obtenu par combinaison d'un complexe de type métallocène neutre selon l'une quelconque des revendications 1 à 7 précédentes et d'un cocatalyseur capable d'en extraire un groupe anionique lié par une liaison sigma.
- 25 14. Catalyseur selon la revendication 13, dans lequel le cocatalyseur est choisi parmi des acides de Lewis aprotiques capables d'extraire un groupe anionique lié par une liaison sigma du complexe de type métallocène neutre pour former un anion non coordinant, et des sels organiques dont l'anion est non coordinant et le cation est capable d'extraire un groupe anionique lié par une liaison sigma de ce complexe de type métallocène neutre pour former un composé neutre.
- 30 15. Catalyseur selon la revendication 13 ou 14, dans lequel le complexe de type métallocène neutre comprend au moins un groupe alkyle ou amide lié au métal M.
- 35 16. Catalyseur selon l'une quelconque des revendications 8 à 15 précédentes, caractérisé en ce qu'au moins un constituant choisi parmi le complexe de type métallocène et le cocatalyseur est supporté sur un support granulaire solide polymère, inorganique ou organique.
- 40 17. Catalyseur selon la revendication 16, dans lequel le support granulaire solide est choisi parmi de l'alumine, de la silice et des silicoaluminates.
- 45 18. Procédé de (co)polymérisation d' α -oléfines, comprenant l'introduction dans un réacteur en charges successives ou en continu d'au moins une α -oléfine et d'éventuels comonomères, et la (co)polymérisation du mélange en suspension ou en solution dans un milieu liquide approprié, ou en phase gazeuse, en présence d'un catalyseur de polymérisation, caractérisé en ce que ledit catalyseur est le catalyseur selon l'une quelconque des revendications 8 à 17 précédentes.
- 50 19. Procédé selon la revendication 18, dans lequel l' α -oléfine est l'éthylène.
- 55 20. Procédé selon l'une quelconque des revendications 18 ou 19 précédentes, dans lequel le catalyseur est formé *in situ* dans le réacteur de polymérisation par mise en contact du complexe de type métallocène selon l'une quelconque des revendications 1 à 7 précédentes avec un cocatalyseur constitué d'un dérivé organo-oxygéné d'aluminium, de préférence d'un aluminoxane.